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Fabrication of Dense MgO

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13. ABSTRACT

Three methods of hot-pressing dense MgO bodies are described. Two of these methods start with MgO powders, one using LiF or NaF additions, and the other, no additions. The third method involves the direct hot-pressing of precursor salts (e.g., $Mg(OH)_2$). The latter two methods use temperatures of approximately 1300°C with pressures of 5000 psi for times of about 15 minutes to assure complete densification. The addition of LiF lowered the pressing temperatures 300° to 400°C, and the addition of NaF, 200° to 300°C. Hot-pressing problems and imperfections in the resulting bodies are discussed to aid in further improvement. The most fundamental problem was removal of the gaseous impurities such as H_2O and CO_2 from the powders. Vacuum-hot-pressing aided some but did not completely remove them. Explosions and lenticular voids are major problems attributed to these gaseous impurities. Other impurity effects on color, most likely due to cation impurities, are also noted. Densification mechanisms are discussed, and the possible effects of gaseous impurities in hot-pressing mechanisms with or without additives are noted. The main effect of hot-pressing with NaF or LiF may be primarily to bring about more intimate contact between particles by enhanced interparticle sliding. The actual sintering mechanism which occurs whether or not pressure is applied is probably diffusion in the region of the grain boundary due to retained fluoride, most likely as a liquid phase.

14. KEY WORDS	LINK A		LINK B		LINK C	
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Ceramics						
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Grain growth						
Porosity						
Surface						
Hot-pressing additives						
Pressure calsintering						
Fabrication						

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CONTENTS

ABSTRACT

Dense bodies of hot-pressed MgO are characterized for impurity or additive (LiF or NaF) contents and changes with subsequent annealing. As-hot-pressed bodies from a variety of raw materials and pressing techniques are shown by ir, mass spectrometry, and weight-loss measurements to contain variable amounts of hydroxides, carbonates, and possibly bicarbonates averaging several hundred parts per million in total content. The gases released in the decomposition of these impurities can cause clouding and bloating of bodies on annealing subsequent to hot-pressing, depending on concentration, specimen size and integrity, and heating rates.

The other predominate impurities, Ca and Si, are observed primarily along triple lines in large grain specimens (i.e., those with substantial annealing after hot pressing). Some of these impurities are also found on grain boundaries in patches much smaller than the grain size. In finer grain-size bodies, much of the Ca and Si also appears to be along triple lines, but some is present as patches that appear to follow grain boundaries over an area of several grains. The size and distribution of these patches are quite irregular. Since the Ca may initially be present as the hydroxide and carbonate, its inhomogeneity may be related to that of the above anion impurities.

Most of the Li and Na which were added as fluorides is lost during hot-pressing. More F than Li or Na remains, indicating that it reacts with MgO. Li, Na, and F contents are all further reduced by subsequent annealing, so that only a few hundred parts per million F are retained in smaller bodies after moderate annealing. Differences in specimen colors for various materials and fabrication methods and changes in color with annealing indicate interaction of additives with impurities and differences in amount or association of impurities. Differences in association or amount of impurities are also indicated by marked changes in surface hydration of some MgO bodies after annealing, and by different impurity structures formed on annealed surfaces in other bodies. Surface scratches are shown to be removed by annealing at or below $1500°C$.

Grain growth data are presented for dense bodies and bodies with a low percent of porosity. Pores in fine-grain bodies are small and predominantly at the grain boundaries. With further grain growth, the pores grow and become located mostly within the grains, approximately as negative crystals.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

FABRICATION OF DENSE MgO

INTRODUCTION

Significant development and evaluation of the polycrystalline properties of MgO have occurred in recent years, primarily through the use of hot-pressing. However, important variations in fabrication results, behavior of bodies, and intepretation of such behavior occur. This report, which summarizes 7 years of fabricating and studying MgO, is presented to aid in further improving its fabrication by more clearly demonstrating the failures and successes encountered. This report also serves as a basis for a second paper on the characterization of hot-pressed MgO (1), part of this characterization report being directed toward an understanding of the cause of many variations in fabrication and behavior. Both of these reports in turn form a basis for a third paper on strength and fracture of hot-pressed MgO (2).

EXPERIMENTAL TECHNIQUE

Fabrication

The reagent-grade oxide or precursor powders which constituted a major portion of the study are shown in Table 1. Some of the FH powder was calcined in 99% pure MgO fused-grain, thin-wall crucibles at 425°C for 1 hour in air or in a sealed metal retort with argon at reduced pressures as previously described for $Ca(OH)_2$(3). Some MBC powder was similarly retort-calcined at 540°C for 0.7 hour.

Additives (all reagent grade) were mixed with some of the powders by milling for 2 hours in a porcelain mill with high-alumina cylindrical grinding media and organic (reagent-grade) solvents. The resulting slurry was dried and the loosely caked material passed through a number 28 screen, then stored in approximately 0.5-pound quantities in sealed jars. In fabricating without additives, the powder was used directly from the supplier's 1-pound bottles, which were kept sealed with tape. Cold-pressing studies were conducted under ambient conditions using a universal testing machine to apply loads at a head travel speed of 0.05 in./min.

Most hot-pressing with LiF or NaF additions was done in induction-heated, single-acting hot-presses open to the atmosphere, while most hot-pressing without additives was done in a vacuum hot-press. Details of the hot-pressing systems and the measuring techniques used have been described in Ref. 3. Most pressings were done in similar graphite dies, with dimensions of 4 to 6 inches tall, 1 to 1.5 inches wall thickness, and 0.001 to 0.005 inch clearance of the ram from the wall, and a few in a similar nickel-base alloy die.* Most pressings with additives were of disks 1.5 inches in diameter and 0.1 to 0.2 inch thick, but some up to 1 inch thick were also made. Pressings without LiF or NaF were 0.2 to 1.2 inches thick with diameters of 1.0, 1.5, and 2.0 inches. In either process, two or three thinner specimens (normally previously cold-pressed in the die with 1000-2000 psi) were usually pressed simultaneously in the same die by using thin graphite spacers between them.

Note: Most of this work was performed while the author was in the Space Division of The Boeing Company, Seattle, Washington.
*Hastelloy B - Haynes Stellite Co.

Table 1
"Pure" MgO Powders Studied

Powder Designation in Article	Approximate Composition	Grade	Source	Descri[	
				Particle Size (micron:	
				Range	Average
M	MgO	Reagent grade	Mallinckrodt Chemical Works, St. Louis, Mo.	0.1-0.3	0.2
MBC	Approximately $MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$	Reagent grade	Mallinckrodt Chemical Works, St. Louis, Mo.	—	—
F	MgO	Electronic grade, low activity Catalog #M300	Fisher Scientific Co. Pittsburgh, Pa.	0.05-0.1	0.1
FH	$Mg(OH)_2$	Reagent grade	Fisher Scientific Co. Pittsburgh, Pa.	—	—
K	MgO	High purity	Kanto Chemical Co. Japan	0.07-1.0	0.2
TTA	MgO	High purity	Oak Ridge (from $MgCO_3$ made by acid digestion of pure magnesium)	0.02-0.4	0.05
G	MgO	Reagent grade	E. Merck AG., Darmstadt, Germany	—	—
DH‡	Mg(OH)	High purity†	—	—	—

*Based on sample electron microscope examination of samples.
†Courtesy of W. A. Sibley, Oak Ridge National Laboratory.
‡Courtesy of C. Williams, Dow Chemical Co.

Analysis

Most analytical techniques and equipment were those in common usage, or as previously described for CaO (3). Mass spectrometer data were obtained by heating samples (about 1 gram) in a tungsten crucible in a Knudsen cell. Heating to 2000° to 2200°C was accomplished in 4 to 7 hours after an initial overnight pumpdown. Grain size was taken to be the average grain intercept length along straight lines on electron micrographs of fracture replicas. Friction tests were made by reciprocal sliding of a "rider" with two flat strips in contact with a flat plate. Wetting tests were made by placing a small pile of powder on an MgO sample, and observing it during melting and subsequent solidification. Silicon carbide resistance-heated furnaces open to the atmosphere were used for these tests and also for firing cold-pressed specimens.

RESULTS

Powder Studies

Particle and agglomerate size data on the oxide powders based on sample electron micrographs (e.g., Figs. 1 and 2) are shown in Table 1. Manufacturers' data, which were available for F MgO, agree well with the particle size measured but reports a finer agglomerate structure: "These oxide particles are agglomerated in an aerogel structure rather than in the more compact hydrogel. Most agglomerates are in the 0.5- to 1.25-micron range...only 0.5% are 10 to 20 microns and none above 20 microns (based on alcohol sedimentation)." K MgO particles had an irregular shape somewhat like those of M MgO (Fig. 1), while the TTA particles were mostly well-shaped cubes like those of F MgO. (Whiskers were observed actually growing perpendicularly to the TTA cube faces during observations at high magnification in the electron microscope.)

Fig. 1 - Electron micrograph of M MgO powder

Thermal gravimetric (TGA) and differential thermal analyses (DTA) were made on the MBC powder, after which the powder was exposed to the air while still in the apparatus. In 9 days, the material regained 4.6% of its weight and showed the subsequent DTA curve of Fig. 3 on being rerun. Mass spectrometer analysis of F MgO powder showed substantial amounts of CO_2, CO, H_2O, OH, along with some O and C, being given off to temperatures of at least 1500°C.

Survey compaction studies, using about a 3-inch die filled with F and M MgO without binders or lubricants, showed that ball milling (in benzene), with or without LiF additions
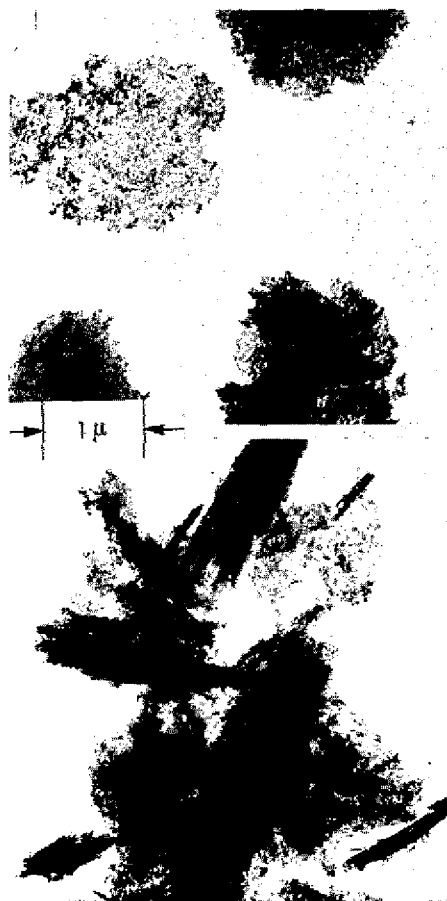
Fig. 2 - Electron micrograph of F MgO powder. Note fibrous agglomerates or particles often found in this powder.
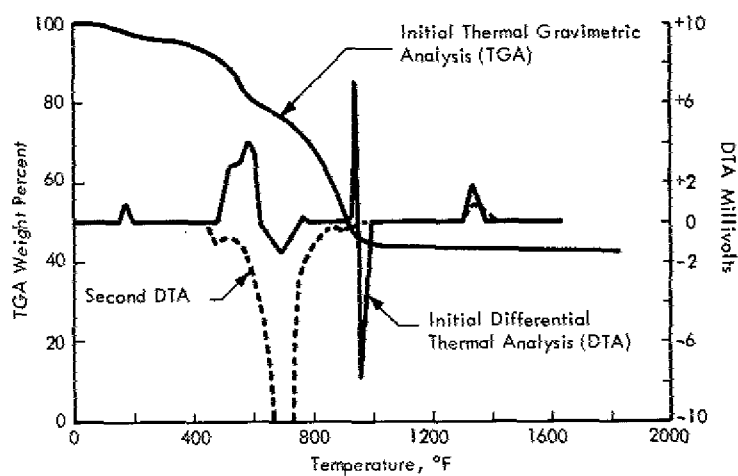

Fig. 3 - TGA and DTA data for Mallinckrodt magnesium basic carbonate. Second DTA run was made after material from first run had remained in apparatus for 9 days (regaining 4.6% of its weight).

or drying and screening, had no observable effect on cold-pressing. Laminations were generally not observed below 5000 psi. Repressing granules obtained by breaking and screening original pressings changed the compaction behavior as shown in Fig. 4, and substantially reduced laminations (ram travel was only about 1.4 inches compared to 2.5 to 2.8 inches for initial pressing). Densities of cold-pressed bodies before and after sintering are shown in Table 2.
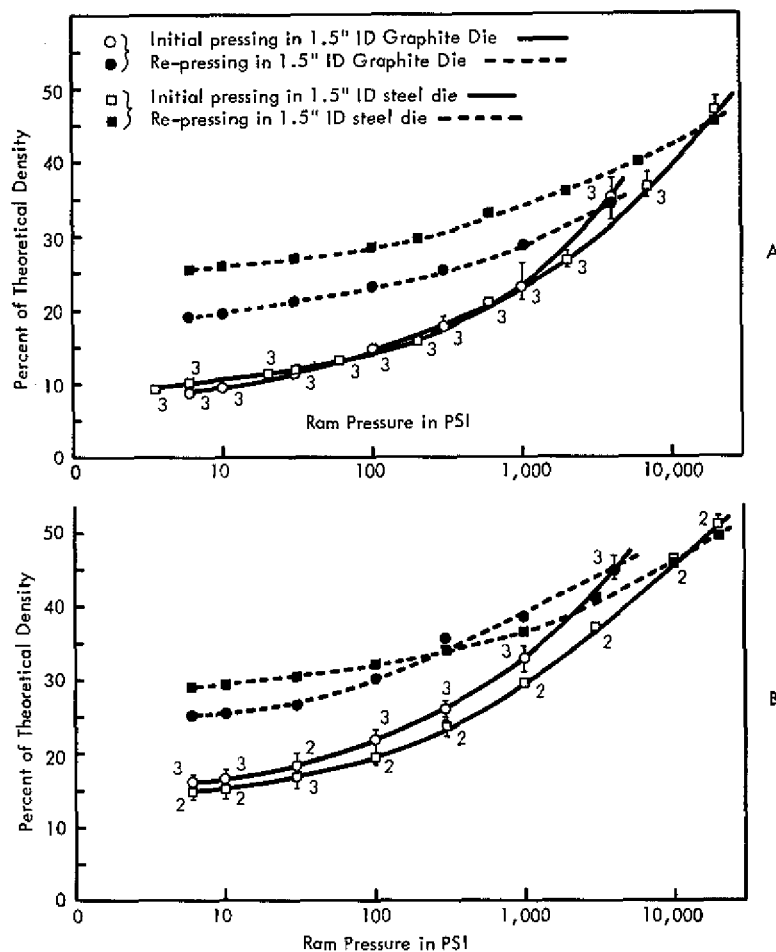

Fig. 4 - Cold-pressing of MgO powders (a) F MgO and (b) M MgO. Vertical bars (often not greater than the symbol height) represent the range of data, and numerals are the number of tests if more than one test was run.

Hot-Pressing With Additives*

Development

Initial work showed that additions of 0.5-w/o LiF substantially improved densities in both hot-pressing and sintering MgO, with hot-pressing clearly producing the highest density. M MgO was superior to other powders not listed in Table 1: 95 to 98+% of theoretical density was achieved even when pressing temperatures were reduced to about 1000°C at pressures of 2000 to 4000 psi. Stirring the milled slurry during the evaporation

*Most of this work is from a previous paper by the author (4).

Table 2
Sintering of Cold-Pressed MgO

Powder	Cold-Pressing Pressure (psi)	Percent of Theoretical Density as:	
		Cold-Pressed	Air-Fired at 2200°F (1205°C) for 1 Hour
Fisher	3,000	30	65
Fisher	3,000	34	55
Fisher	4,000	34	66
Fisher	20,000	45	91
Fisher	30,000*	50	91
Fisher + 2-w/o LiF	20,000	45	97
Mallinckrodt	3,000	41	75
Mallinckrodt	4,000	44	65
Mallinckrodt	20,000	50	79
Mallinckrodt + 2-w/o LiF	3,000	41	94
Mallinckrodt + 2-w/o LiF	20,000	49	97

*Isostatically pressed.

of the organic fluid generally eliminated the opaque regions that had occurred in previous hot-pressed specimens. Simply decanting excess liquid and drying in a stainless-steel tray in a warming oven was later found adequate to prevent these opaque regions when 2-w/o LiF additions were used. Reagent-and technical-grade acetone, ethyl alcohol, isopropyl alcohol, benzene, and cyclohexane were used for milling with no obvious differences among them, except the milled powder settled out of the nonpolar fluids very rapidly.

Specimens were often highly fractured when hot-pressed in contact with ATJ graphite rams or spacers. This problem was reduced by releasing ram pressure at the start of cooling, coating spacers with MgO without additives, or polishing spacers on a paper towel. Use of graphite cloth as spacers eliminated this problem and gave good specimens; therefore, this cloth was used for about half of the work. Pyrolytic graphite spacers were later found to prevent sticking and cracking as well, besides eliminating the need to grind the cloth pattern from the MgO. They were used for most of the remaining work.

Conditions selected for normal fabrication were hot-pressing with 2-w/o LiF in a graphite die at 1000°C. During the approximately 20-minute heating period, a pressure of about 100 psi was maintained on the ram. This required considerable pumping of the hydraulic jack above 650°C because of rapid compaction, as shown in Fig. 5. The pressure was increased to about 3000 psi at the pressing temperature and held for 5 minutes, then the induction power was turned off and the pressure released during initial cooling. Thicker bodies (e.g., 1 in. thick after hot-pressing) were hot-pressed at 3500 to 5000 psi for 15 minutes.

Hot-Pressed Body Description

At least 75% of the 200 or more M MgO specimens fabricated under the above conditions were 98% or more of theoretical density and uniformly translucent, such that typical book printing could be located and often read through a piece about 0.1 in. thick sitting
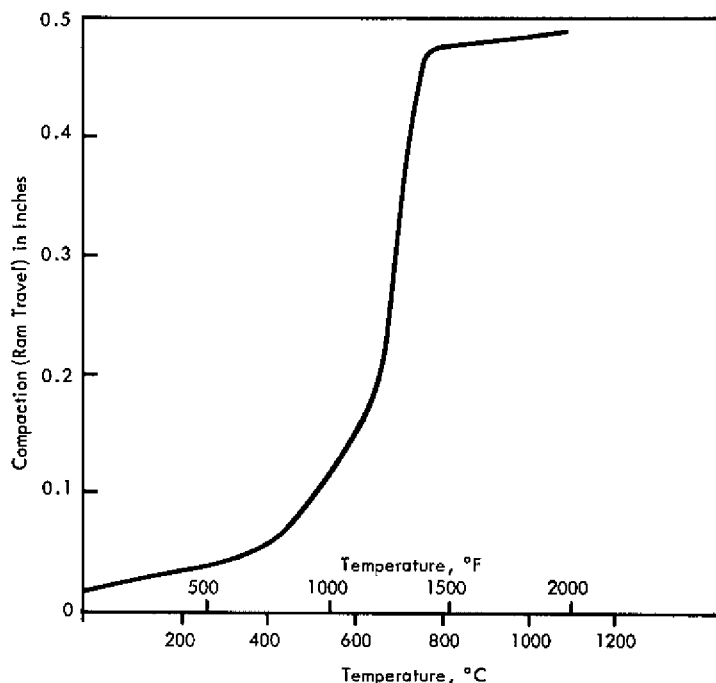
Fig. 5 - Compaction of Mallinckrodt MgO with 2-w/o LiF
versus temperature. The test was run in a graphite die
under a pressure of 1600 psi with an approximately linear
heating rate of about 100°F/min.

on the page. Colors were fairly uniform in a given specimen, but for different specimens
the colors ranged from a light milky appearance with some gray tone to a definite gray-
blue color to a light (but clearer) gray color. Grain size was typically 0.5 to 2.0 microns.

Most specimens not falling in this group were characterized by either dull, opaque
black color or by laminar voids (Fig. 6a). Such voids appeared to be most common when
pressure was applied at a lower temperature, especially in thicker specimens. Black
specimens appeared to be most common with possible earlier inadequate cleaning of
graphite dust from the dies.

Temperature-Time-Pressure Parameters

Translucent disks could be obtained at temperatures as low as 925°C and with higher
pressures (e.g., about 5000 psi) and longer times (e.g., 15 min). No differences were
observed in limited pressings done in a resistance-heated furnace which took 2 to 3 hours
to reach temperature. Clearer, grayer specimens appeared to be more common at pressing
temperatures above 1040°C. Higher pressures appeared to increase the compaction rate
of Fig. 5 only a small amount.

Additives

With adequate mixing, little difference was observed between specimens made with
1/2-, 1-, or 2-w/o LiF, except possibly slightly easier compaction and better uniformity
with 2-w/o LiF. Several disks hot-pressed with 1-w/o LiF and 1-w/o LiCl appeared the
same as those made with 1-w/o LiF only, but on sitting in the atmosphere for several
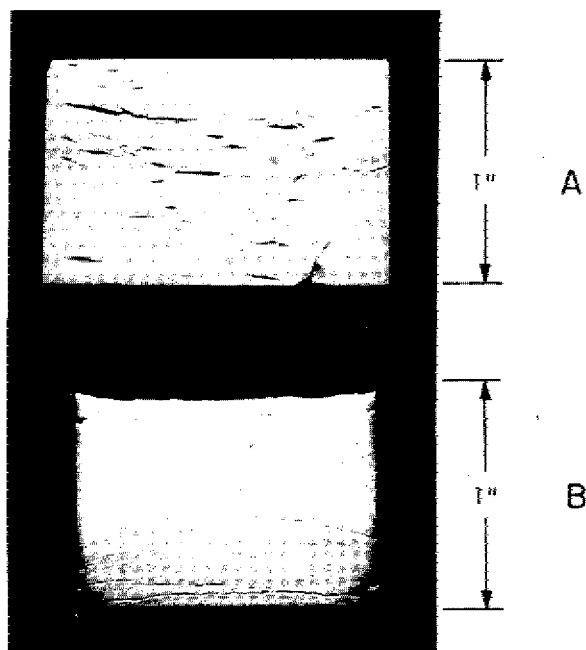weeks, they developed a distinctly "wet" surface. Darker gray to black specimens resulted

Fig. 6 - Laminar voids in hot-pressed bodies: (a)
M MgO hot-pressed with 2-w/o LiF and (b) MgO
vacuum-hot-pressed without additives. Note, top
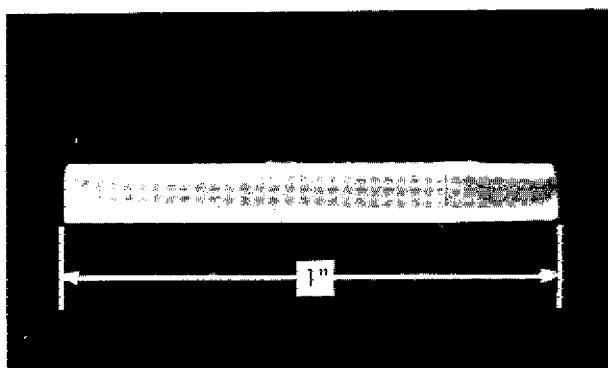was off due to "delamination."

Fig. 7 - M MgO + 4-w/o LiF hot-pressed between M
MgO powder without LiF. Note that the dense outer
MgO remained white, but most of the MgO + LiF
inside was black after hot-pressing.

in the few pressings with 4-w/o LiF (Fig. 7). Trial hot-pressing of M MgO with 1-w/o
and 2-w/o NaF showed that temperatures of about 1040°C or more were required to
obtain translucent specimens (which were also gray-blue in appearance) at pressures of
about 4000 psi for 90 minutes. Bodies pressed with 2-w/o NaF were somewhat more
translucent than those pressed with 1-w/o NaF but less translucent than bodies made with
LiF.

MgO bodies with 1- 5- to w/o additions of other oxides (Al_2O_3, CaO, and NiO) were
also hot-pressed using 2-w/o LiF under typical conditions for MgO with LiF only. A

1-w/o Al_2O_3 addition generally increased translucency (more gray than blue) but often resulted in black specks in the disks. Results appeared to be the same for several sources of both alpha (Linde A) and gamma (Alon C) Al_2O_3. MgO with 5-w/o CaO additions was a fraction to a few percent less dense than without CaO (slightly translucent gray to opaque white, respectively). Specimens with 2-w/o NiO were completely black to a depth of about 1/4-inch or more. Trial hot-pressing of NiO using LiF indicated no benefit from the LiF.

Raw Materials Variation

F MgO was found to work as well as M MgO and had about the same appearance. For either powder, some lots resulted in more consistent, or a greater degree of, translucency than other lots. The material appeared to age once opened to the atmosphere, and longer exposure increased the tendency toward black or less translucent specimens. However, exposure to 100% relative humidity at 40°C for up to 1 month did not appear to change the resultant densification or transparency of the material. Hot-pressing of M MgO powder, calcined before or after addition of LiF, to 750° to 1000°C typically resulted in poorer (and often black) specimens.

Hot-pressing MBC powder calcined in a retort with an air leak resulted most commonly in black specimens or in gray specimens with black spots often having many laminar voids, while hot-pressing of MBC powder calcined without atmospheric contamination resulted in specimens approaching, but not equal to, the quality obtained with M MgO. Use of FH powder calcined in air usually resulted in gray-translucent specimens with white laminar "speckles." A trial of K MgO with 2-w/o LiF at 1040°C with 7500 psi for 20 minutes resulted in an opaque body which "delaminated."

Pressing Environment

Use of filter paper, which charred, leaves carbon powder and flakes in contact with specimens and results in a dull black layer up to 0.050 in. or more thick with M MgO (and M MgO + Al_2O_3), while less effect was indicated in cursory tests with F MgO. Use of metal foils made of nickel, mild steel, or stainless steel in graphite dies or pressing in the metal die usually resulted in completely opaque disks of a gray-to-blue appearance for M MgO and M MgO - 1-w/o Al_2O_3. The reaction between the metal die and the MgO-LiF powder was limited in depth, but the metal foil and specimen were often bonded together resulting in considerable cracking in the MgO. Use of a graphite cloth in the metal die resulted in translucent specimens like those pressed in graphite dies (without metal foils). A few pressings were also made using hot-pressed boron nitride spacers resulting in very poor gray-to-black specimens having many laminar voids. Limited vacuum-hot-pressing trials did not appear to make significant differences in the behavior of the material during pressing, or in the resultant body.

Extrusion

Observations of some lateral flow in cylinders from dies broken during hot-pressing, or sagging if bars were annealed while supported near the ends of their faces rather than their sides, showed that MgO + LiF was somewhat plastic at elevated temperatures. This suggested that "hot extrusion" or "forming" was feasible. Some back extrusion was readily accomplished (Fig. 8) by placing previously hot-pressed MgO + LiF cylinders in a die and using a moving (top) ram bored out along the axis with a tapered entrance.
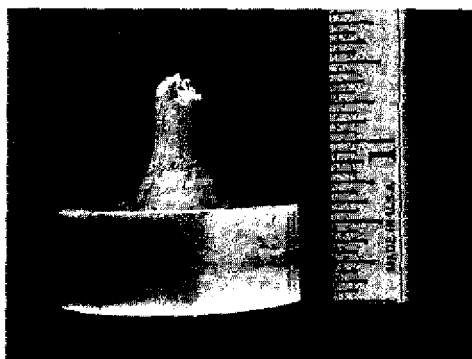
Fig. 8 - "Hot extrusion" of a dense M MgO
body hot-pressed with 2-w/o LiF. This back
extrusion was at 1035°C and an area reduc-
tion ratio of about 16 to 1 using a pressure
of about 4000 psi. The extrusion rate was
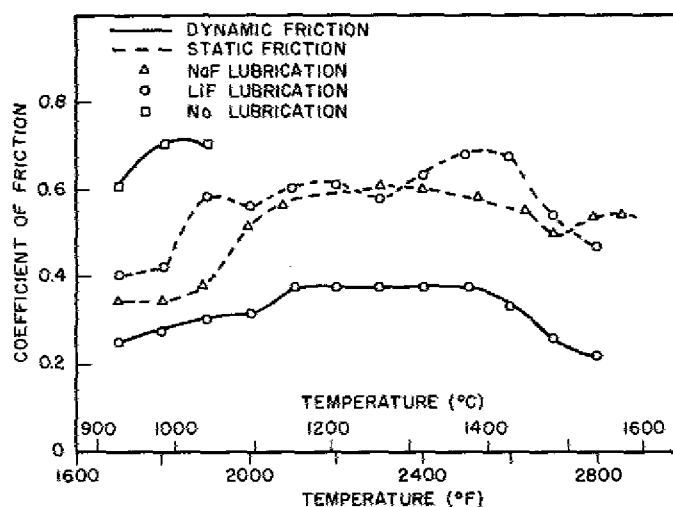about 0.05 in./min.

Fig. 9 - Coefficient of sliding friction between {100}
surfaces of MgO crystals at 640 psi. Dynamic friction
measurements were made using oscillation at 60 cycles/
min over an amplitude of ±0.125 in.

Wetting and Lubrication

LiF and NaF spread over the surface wetting both single and polycrystalline MgO.
Lubrication results are shown in Fig. 9.

Fabrication Without LiF or NaF

Cursory Experiments

Cursory experimentation with F and M MgO based on the above experience and on
data of Spriggs and Vasilos (5) showed that translucency could generally be obtained at
about 1250°C or more with pressures around 5000 psi for times at temperature and
pressure of 5 minutes or more. A few trial hot-pressings of M MgO without vacuum were
fairly successful but indicated some advantage of vacuum-hot-pressing which was used for
all further work.

Limited experimentation indicated that densification during hot-pressing progressed
more slowly in dies filled with loose rather than cold-pressed powder. Powders typically
underwent ten-to twentyfold reductions in height in the die from loose fill to full density,

and four- to fivefold from the cold-pressed height, limiting final lengths to about 1.0 and 1.25 inches respectively for F and M powders. A longer cylinder was successfully made by hot-pressing an isostatically pressed body of F MgO dry-machined to fit the die. Boundaries between successively cold-pressed layers were fairly well bonded but were usually visible and showed some evidence of laminar patches at the interfaces after hot-pressing, even when the cold-pressed surfaces had been thoroughly cleaned and broken before cold-pressing another layer of powder on them. Therefore, thick parts were normally loaded by cold-pressing the complete specimen at once using two or three stacked dies.

During heating in the vacuum-hot-press, distinct outgassing peaks were observed (Fig. 10). These varied some in height and location with the rate of heating but appeared to have some consistency for a given type of powder. The rate of compaction was always at a maximum in the region of such peaks. Limited trials in which ram pressure was applied below this peak generally gave less dense specimens. Maximum transparency was generally obtained by applying ram pressure on the "down-hill" (high-temperature) side of this peak instead of waiting until the pressing temperature was reached. This also increased mean grain sizes to about 3 to 7 microns. Application of pressure before or during this outgassing peak frequently resulted in clicking or snapping sounds (transmitted through the pressing train) which were often accompanied by short but substantial rises in chamber pressure, especially with thicker specimens. Resultant specimens often had thin laminar voids (Fig. 6b), which were generally greater in number with more of the above sounds and pressure rises during hot-pressing.
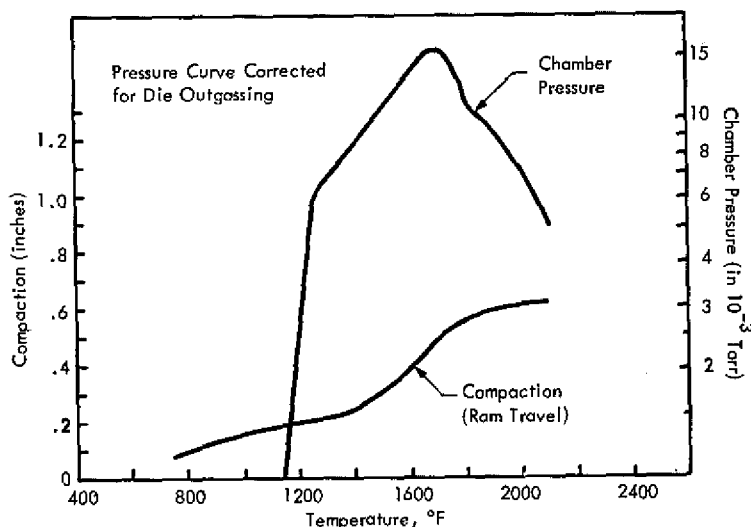

Fig. 10 - Outgassing and compaction of F MgO during vacuum-hot-pressing (ram pressure 3000 psi)

In a few cases with large billets, actual explosions occurred in which the die was broken in three or more pieces; MgO powder and fragments were scattered in the chamber; and a sharp transient rise in chamber pressure occurred. This appeared to occur more commonly with F than with M MgO. On the other hand, delaying the application of pressure to 1300° to 1400°C resulted in the powder shrinking away from the die, often resulting in poorer specimens. The majority of specimens were therefore pressed with pressure started at 0° to 50°C below pressing temperatures which were usually 1250° to 1350°C. Most other specimens had pressure applied about 1100°C or higher. Cursory trials in which the die and powder were preheated to 500°C or more in the vacuum-hot-press for outgassing, then cooled prior to normal heating for hot-pressing, generally resulted in white, somewhat porous and opaque specimens.

Hot-Pressed Body Description

The transition between the white opaque appearance when densification was incomplete and translucency in F and M MgO as full density was approached often occurred as a central lenticular translucent region (Fig. 11) which increased in size as the pressing conditions were increased. Translucency in M MgO was less homogeneous and usually did not extend completely to the full diameter, while translucency in F MgO was more homogeneous and would become clear over the whole disk. Sometimes there were also translucent rings inside an opaque rim in M MgO. When specimens were pressed near the bottom on the die, and hence in a temperature gradient, the top was often the only portion to become translucent for either material. Translucent F MgO could generally be obtained at somewhat lower temperatures than could M MgO.

The above observations of fair translucency developing from the center outward with increasing pressing parameters allow an outline of conditions just necessary to achieve translucency over a complete disk of F MgO to be made. Complete translucency over the complete specimen indicated that pressing conditions were just adequate or greater than necessary. On the other hand, when the translucent region was smaller than the specimen, conditions were inadequate. As shown in Fig. 12, these upper and lower bounds agreed very well with few exceptions. The few specimens found whose translucent region was just approaching the complete cross section, indicating conditions just sufficient for full translucency, fell between these upper and lower bounds as expected. This figure shows clearly that higher temperature could be interchanged for shorter times and vice versa. Some reduction in pressing time or temperature could also be achieved by using higher pressure. However, significantly finer grain sizes could not be obtained by reducing temperatures and/or times by pressing at 10,000 psi.

Fig. 11 - Final internal densification of FMgO. The specimens were vacuum-hot-pressed (at 5000 psi) as shown at the right. The dumbbell-shaped band was fairly common, especially in larger diameter pressings. Such internal transparent regions were normally a light yellow color in F MgO.
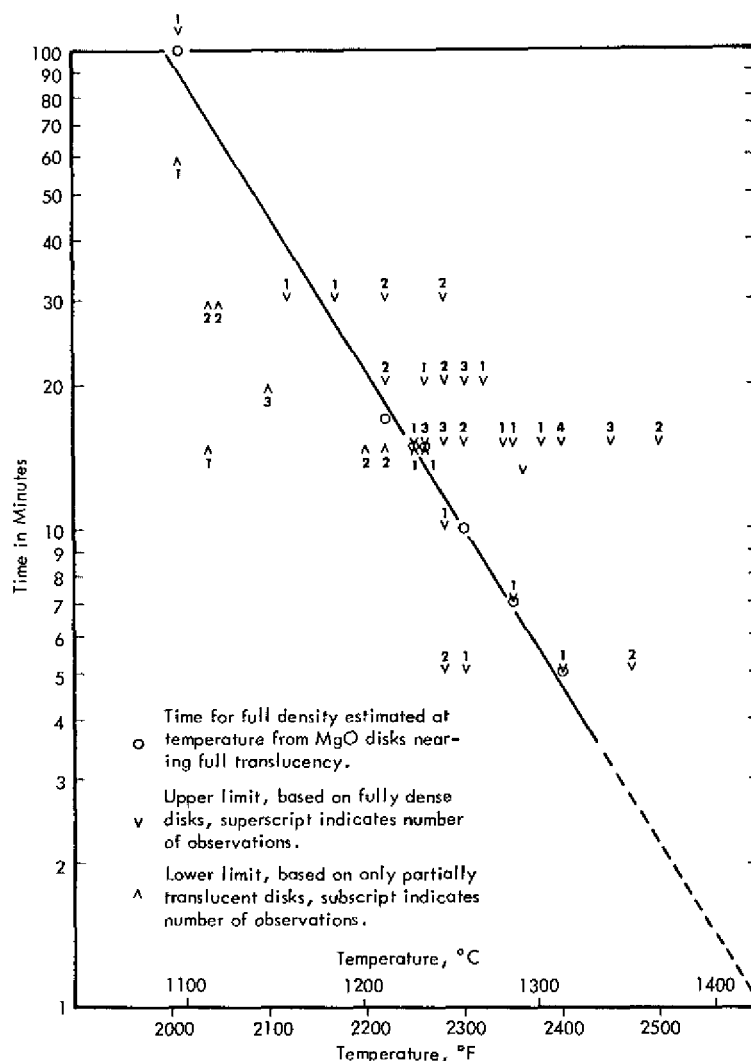
Fig. 12 - Fisher MgO densification time versus temperature for complete densification of 0.25-in.-thick disk (1.5-2.0 in. diameter) at 5000 psi

A fraction of the 200 to 300 specimens fabricated had very gray to black sections, opaque white laminations, or thin laminar voids (more frequent in thick specimens). All appeared to occur more frequently in F than in M MgO.

Typical as-hot-pressed grain sizes of F MgO were 1 to 4 microns while those of M MgO were 3 to 8 microns. It was difficult to get the finest achievable grain size at full density with much consistency in either material, and there were often variations of twofold or more in grain size in a given pressing.

Repressing

Hot-pressing with 5000 psi for 15 minutes at 1050° to 1200°C resulted in densities from 2.34 to 3.57 g/cc with an indication of more scatter in density at these lower temperatures. Subsequent repressing of several of these disks with pressures of 5,000 to 10,000

psi for 15 to 30 minutes with temperatures of 1200° to 1320°C substantially increased densities. Six of twelve such repressed disks were translucent or had translucent areas. However, if partially pressed disks were slowly air-fired to about 1100° to 1200°C for 1 hour before subsequent repressing, final hot-pressing densities were increased less. Only one translucent disk was obtained in eight trials under repressing conditions comparable to or more favorable for translucency than above. Grain sizes averaged about 2 to 3 microns (about the same for normal hot-pressing) for repressed specimens whether or not they had an intervening firing.

Two partially hot-pressed F MgO disks were used as spacers on either side of some M MgO powder. Hot-pressing with 5000 psi at 1260°C for 20 minutes resulted in complete translucency in the F MgO, and partial translucency (mostly in the center) in the M MgO. The joint between the three was visible but appeared to be sound, even after diamond sawing and grinding.

Die Materials

A few trials of hot-pressing were made using dense hot-pressed Linde A Al_2O_3 spacers. F MgO showed no bonding to the Al_2O_3 to temperatures of at least 1260°C, but the M MgO showed some definite bonding.

Other Powders

Limited trials of vacuum-hot-pressing of calcined FH powder with 5000 psi at 1315°C for 45 minutes produced gray, translucent disks with numerous opaque white and gray laminar speckles. Poorer results were obtained with calcined MBC powder.

K MgO had about 18% porosity after vacuum-pressing with 5000 psi at 1315°C for 15 minutes. Repressing in vacuum with 5000 psi for 15 minutes at 1425°C and again at 1485°C left about 2.5% porosity. The final bodies showed some "laminar" cracks 0.25 to 0.5 in. in diameter, along with irregular laminar translucent patches up to 0.3 in. in diameter in a white opaque matrix (Fig. 13). Raising pressures to 10,000 psi and times to 45 minutes resulted in a opaque and severely laminated bodies. Trials with the TTA powder were similar but laminations did not seem as severe and the body had a more opaque matrix (e.g., due to an overall porosity of 7%) with fewer translucent lenticular areas (mostly in the center two-thirds of the body).

Fig. 13 - Translucent lenticular areas in an opaque matrix during trial pressing of Kanto MgO. Final overall porosity was approximately 2.5%. Note shallow dish-shaped fragments missing from the surface due to delamination. Cross section was approximately a 0.1-in.-thick specimen.

Vacuum-hot-pressing of G MgO powders at about 1260°C resulted in a translucent central area separated from an outer opaque area by a brown ring. Hot-pressing over 1300°C resulted in larger (now gray to black) central areas and rings.

Direct vacuum-hot-pressings of FH, DH, and MBC powders without prior calcining were conducted following the procedures of Morgan (6) and Chaklader (7). FH and DH

powders pressed to a gray translucency (like that of F MgO) in disks about 0.1 in. thick with 5000 psi at about 1200° to 1300°C, usually for 15 minutes. A pressure of 2000 psi was generally maintained throughout heating until full pressure was built up over about a 50°C range, about 100°C below pressing temperature. Vacuum-chamber pressures were significantly higher than for pressing of MgO powder only during heating when the temperature was below about 1000°C. FH powders produced bodies with fine lenticular "speckles" about 0.05 in. in diameter, while bodies from DH powder had fewer, but larger, speckles. Both of these materials also produced translucent bodies which had a gray tint, mostly due to a thin gray surface, with DH bodies having darker, thicker gray areas. Thicker DH specimens had a thick orange-pink central region which increased as the gray surface thickness decreased with decreasing pressing temperatures. Making thicker specimens, with lower temperatures, showed that translucency developed first near the outside and expanded inward with increased time or temperature.

A few trial direct pressings of MBC powder (which also outgassed mostly below 1000°C) generally produced a porous, white, opaque body with the "mud-cracked" appearance of Fig. 14 with only low pressures between 100 to 300 psi during heating. Higher pressures during heating could produce a variety of results, from translucent specimens with opaque lines (like collapsing the above "mud-cracked" structure) to mixed translucent (very light gray) and white opaque sections, to a translucent ring near the periphery with a white opaque core (the last appears more common in thicker specimens).
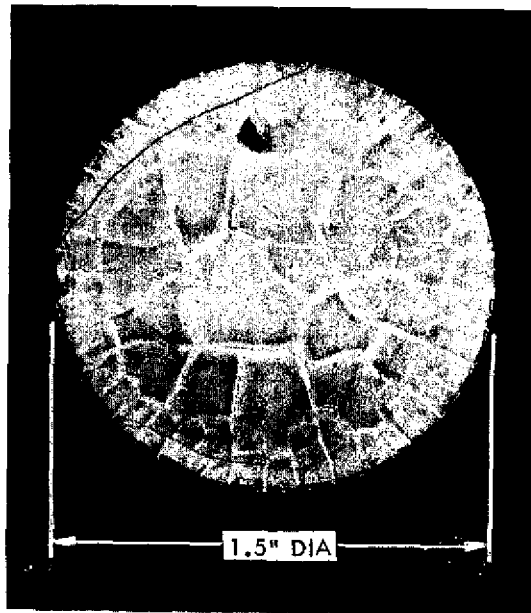

Fig. 14 - Mud-cracked pattern on a specimen vacuum-hot-pressed directly from MBC powder

DISCUSSION

Defects

The observed explosions in larger specimens (more commonly in F MgO) are consistent with the outgassing of MgO and the difficulty of gases diffusing out of bodies with fine porosity. Recently, the author and G. Friedman (8) showed that M MgO plus 2-w/o LiF powder, tamped to only 20 to 30% of theoretical density in a 12-inch tube of 0.5-square inch cross section, so restricted diffusion of air from an open end to a vacuum system at the other end, that vacuum pressures of about 50×10^{-3} torr were maintained by

pumping on the open tube (9). Some die failures with MgO plus LiF may also have been caused by such explosions going undetected due to the lack of a vacuum chamber and extensive specimen fragmentation. Similar, but more frequent, explosions have also been observed in hot-pressing CaO (3).

Snapping sounds, outgassing pulses, and laminar voids are due to gases trapped in the body in insufficient quantities to cause explosions. The breadth of these voids in MgO plus LiF and the plasticity of such bodies, as shown by extrusion, are inconsistent with laminations. The cold-pressing data also show that laminations, at least in the number sometimes observed, are unlikely. However, gas bubbles formed during pressing would be flattened by pressure, with some of them probably being squeezed out of the body to cause the snapping sound and pressure rise. On the release of pressure, bubbles could expand to become thicker in bodies as plastic as MgO plus LiF, or lead to delamination in weaker bodies. Some bubbles may be related to laminations, especially between separate cold-pressings, since these would provide pockets for gas expelled from the powder, with the gas, in turn, preventing the elimination of the laminar area. The specks seen mostly in calcined or non calcined MBC and FH specimens may be finer bubbles.

Most, if not all, of the gases are from the starting powders rather than from any reaction with the graphite die, since they also occur when pressing in a metal die and the powders clearly show outgassing in the mass spectrometer in the absence of graphite. Substantial pickup of gases, as indicated by the calcined MBC weight gain, would also explain the aging and lot-to-lot variation of powders. The lack of these problems, at least in specimens 0.25 in. or thinner, made from direct pressings of DH, FH, and MBC powders, appears to be due to their outgassing occurring mostly below 1000°C where they are still fairly porous. Thicker specimens, or higher initial pressures, may result in problems.

The bonding of MgO plus LiF specimens to graphite spacers appears to be a result of simple mechanical gripping due to conformity to surface irregularities since smoother surfaces of polished or pyrolytic graphite eliminated this bonding. On the other hand, M MgO bonded to Al_2O_3 spacers, while F MgO did not. This bonding must be due to impurities in the M MgO since its larger particle size and somewhat lower sinterability make it the least likely to bond by normal reaction or sintering of MgO and Al_2O_3.

Black specimens apparently result partially from graphite and carbon powder, but generally not from graphite cloth. However, the occurrence of such black specimens in the metal die and their apparent greater occurrence with BN spacers, calcined MBC, prefired MgO plus LiF, MgO mixed with 4-w/o LiF, and central areas of G MgO specimens hot-pressed over 1300°C show material and possibly previous environmental causes.

The prevalent gray or gray-blue color of most hot-pressed specimens also occurred in specimens pressed in the metal die and thus is not due to graphite contamination. Further, M MgO hot-pressed without additives has less coloring than when hot-pressed at lower temperatures with LiF. These observations, and the gradiation from gray outside to an orange-pink core in thick DH specimens, show that the gray color must be caused by some impurity in the powders that is affected by both graphite and iron or nickel-based materials.

Densification Without LiF or NaF

The marked increase in compaction of MgO without additives coupled with the marked increase in outgassing suggests a definite association between the two. This relationship is corroborated by similar effects in other materials such as CaO (3) and Al_2O_3 (10). Since the material is mostly MgO and there is at most only a few weight-percent of gas released, and much, if not all, of this comes from crystal surfaces, it is unlikely that any major crystal structure changes such as the collapse of skeletal structures are occurring. It seems much more likely that the gases being given off aid interparticle sliding. This could occur

through a "gas-bearing" effect between particles or by aiding the breakdown of agglomerates. The gas pressures demonstrated by explosions and laminar bubbles show that adequate internal gas pressures may be developed for such effects.

The greater transparency generally achieved by applying pressure below the pressing temperature then appears to be due to taking advantage of such improved consolidation. However, the danger of explosions or bubbles also is greater, and the larger grain size must be at least partially due to the longer total time under pressure.

The occurrence of final densification of MgO powders progressing from the inside outward, rather than from the outside inward, may not be consistent with conventional sintering since temperatures inside the body lag behind those on the surface. The occurrence of hydroxide and carbonate impurities and their stabilization as liquid phases discussed in a subsequent report (1) suggest the same possibility as discussed for similar phenomena in CaO (3). Briefly, such liquid phases would be more concentrated in the center (unless squeezed out during final densification) because of easy decomposition and loss near the surface. Outward migration of impurities is suggested by the brown ring separating the central translucent region from the outer opaque area of G MgO.

The temperature-pressure range of stability of such liquids is not well determined; for example, equilibrium conditions for Brucite range from about 600° to 1000°C (9,11-13) with about 810°C being more recent (14). With pressures of approximately 46,000 psi, stability to 1000°C is indicated (14). Such pressures could exist locally, such as between grains bridging voids. Further, impurities, e.g., Na (15), can extend the range of stability. Thus, a liquid phase due to hydroxyl impurity could aid early densification (e.g., by providing lubrication for interparticle sliding). Carbonate impurities should extend stability to substantially higher temperatures. Because of this, and solubility of MgO in some of these liquids (16), liquid-phase sintering would be feasible.

Such an impurity liquid-phase mechanism would be consistent with poorer results from the preheating of loaded dies in vacuum, and the repressing after annealing, since both reduce gaseous impurities and do not appear to make other changes (e.g., no apparent increase in final grain size). Cold-pressing would help retain more gaseous impurities so the indicated faster densification with cold-pressing could corroborate this mechanism; however, cold-pressing may also be effective by providing closer particle contacts, or increasing thermal conductivity of the powder. The amount, and possibly the ease of formation, of such liquid phases may be another factor in the lack of consistently easier densification with finer particle or agglomerate sizes.

Densification of hydroxides and probably MBC powder, directly hot-pressed, progresses inward from near the outside. This need not contradict the above mechanism, since liquid-aided densification may require a sufficiently low concentration of impurities. A lower concentration would be achieved first in the outer portion of hydroxide and MBC pressings if they retain an excess of such impurities. This would also be consistent with the dense dumbbell-shaped regions (Fig. 11d) in larger-diameter pressings, and the variations of mud-cracked appearance in MBC specimens.

The occurrence of lenticular areas of translucency in an opaque matrix in pressing K or TTA MgO powders which have substantial outgassing (e.g., H_2O) also further corroborates the concepts of such impurity-aided densification and that such densification may depend substantially on local concentration. Similar translucent lenses were observed in hot-pressing Al_2O_3, and again they were smaller in size, greater in number, and more inhomogeneously distributed in bodies made from powders showing the greatest outgassing (17). Thus, the possibility of a liquid impurity phase contributing to densification should be considered in evaluating pressure-sintering mechanisms. This possibility may also be an important factor in the failure of densification models to fit hot-pressing data.

The temperatures used here for the direct hot-pressing of precursor salts (pressure calsintering) are higher than reported by other investigators (6,7). It is possible that some

of these pressings could have been done at somewhat lower temperatures, if precursor salts had been specially selected or prepared. However, both the smaller specimen size and the higher pressures usually used in other pressure calsintering work are probably major factors in the lower temperatures used there. The importance of specimen size is indicated by the change in size of the translucent region with temperature-time changes. Further, greater anion impurity retention (especially OH⁻) occurs at lower pressing of such salts (1). Thus, while pressure calsintering offers some advantages, the exact extent of these requires more detailed verification, with specimen size being an important variable to be considered.

Densification with LiF and NaF

Since the original paper by the author (4) on making MgO with LiF, a number of investigators have used or further developed the process (18-21), often with observations on possible mechanisms. Though the one or more mechanisms involved have not yet been clearly established, some observations on the most likely ones can be made with the advantage of further data and prospective. Several facts must be explained by any proposed mechanisms. First is the enhancement of densification by NaF, but at higher temperatures than for LiF and not as effectively as with LiF. Second is the ready loss of the alkali metal indicating formation of MgF_2 (1,3), which was also discussed by Miles et. al. (18) and reported by Ludekens and Welch (22). Third is the presence of a liquid phase (842°C for pure LiF (23)), which Miles et al. (18) note can be formed about 750°C from LiF and MgF_2. Fourth is the rapid consolidation observed between 600° and 800°C (Fig. 5). This was observed by Benecke et al. (20), who also reported that this range is raised to 700° to 900°C by prefiring MgO plus 2-w/o LiF bodies to 1400°C before hot-pressing. Fifth is the enhancement of sintering in the absence of pressure (Table 2) which is greater than that originally reported by Atlas (24).

Enhanced sintering with LiF suggests that hot-pressing does not introduce any significant new mechanisms but aids or enhances those occurring in the absence of pressure, for example, by bringing particles closer together. The ranges of rapid consolidation at lower temperatures of MgO with LiF, MgO without additives (Fig. 10), and MgO hot-pressed directly from $Mg(OH)_2$ (6) probably result from enhanced interparticle sliding. The extrusion of MgO plus LiF (Fig. 8) certainly shows that such sliding is feasible. The progressive spreading of LiF over grain surfaces by volatilization and condensation above about 575°C (20) may speed the release of physically and chemically adsorbed H_2O and CO_2 to further aid interparticle sliding at lower temperatures, as indicated in outgassing of MgO hot-pressed without additives. The greater regularity of achieving good transparency in specimens hot-pressed with LiF after subsequent annealing (1) indicates that fluoride additives aid in reducing hydroxides. The higher temperatures for densification with NaF would be consistent with higher vaporization and reaction that would be expected from its higher melting point (988°C (23)). Such interparticle sliding should also make plastic deformation of particles which Benecke et al. (20) suggested more feasible since such sliding would relax grain boundary constraints on slip and thus not require operation of all slip systems.

The additives may improve actual sintering by enhancing diffusion. However, as suggested in the similar case of CaO (3), enhanced diffusion is more likely due to solution of F than of Li or Na, because of the greater quantity of F retained. Further, powders such as M MgO which initially contain about 0.5% Na compounds to start with do not show enhanced densification, and Na⁺ does not fit very compatibly in the lattice (in fact, Ludekens et al. (22) report that a noncubic $NaMgF_3$ compound is formed), yet NaF also aids densification. The fact HF and NH_4F aid the densification of MgO (25), that LiF enhances the densification of MgO (25) Al_2O_3 (17), Y_2O_3 (26), and $BaTiO_3$ (27) all

indicate that fluorine substitution for oxygen is occurring since the match of these anion sizes is much better than the match of cation sizes.

Authors considering mechanisms have all suggested that any enhanced diffusion is probably across a thin grain boundary layer. Fluoride phases are probably concentrated mostly at or near grain boundaries where they are found at room temperature in CaO (3) and MgO (1). Enhanced diffusion across such a boundary phase may not depend a great deal on whether the phase is liquid or not. Clearly, substantial transport, whether through a liquid or solid phase, is occurring across the grain boundaries because resultant hot-pressed grain sizes are ten-to twentyfold times starting particle sizes. Since MgO may have some limited solubility in molten LiF and NaF, especially if some MgF_2 and possibly some CaF_2 are formed (28-30), liquid-phase sintering is feasible.

The observation that MgO additions react with fluorine impurities in BeO to form MgF_2, which enhances densification and degrades mechanical properties in the liquid-phase range, supports both the reaction and liquid-phase concept (31). The fact that LiF additions to MgF_2 result in high-density bodies at temperatures of about 680°C while temperatures of about 960°C are required for similar densification with ZnF_2 additions or no additives also indicate that a LiF-MgF_2 eutectic liquid is formed (32).

Actual sintering experiments have been conducted well past temperatures necessary for any liquid-phase formation, and densification is clearly enhanced. Further, grain growth appears to be greater than usual because resulting grain sizes with LiF are about the same as those of comparably dense bodies made without LiF at temperatures about 200° to 300°C higher. During subsequent annealing of hot-pressed bodies, enhanced grain growth is clearly shown in specimens made with fluorides (1) and some further sintering appears to occur.

The water forming on the surfaces of specimens made with LiCl may be due to some LiCl remaining since it is deliquescent (6).

SUMMARY AND CONCLUSIONS

With proper selection of the source and lot of starting materials, dense translucent-transparent MgO bodies can be made by hot-pressing with LiF or NaF additions or without such additions. LiF lowers temperatures for hot-pressing dense MgO 300° to 400°C and results in some plasticity that shows promise for forming more complex shapes. NaF lowers pressing temperatures 200° to 300°C, but limited trials did not produce specimens as clear as those with LiF. Conditions for pressing translucent-transparent MgO without LiF or NaF were typically 1300°C, 5000 psi, and for 15 minutes. Generally, one or two parameters could be lowered by increasing the other(s), with time showing an exponential relationship with temperature for full density at 5000 psi. Greater transparency could be achieved by earlier application of pressure, but at the expense of greater grain growth and chance of explosions. The latter were caused by release of gases and are best avoided by delaying the application of pressure until after most of the outgassing has occurred (typically this was a maximum between 700° and 900°C depending on material, heating, etc.). Thin laminar bubbles could occur due to trapping of gases; thicker ones were similarly observed in MgO made with LiF. Such gas problems increased with thickness and were reduced, but not eliminated, by vacuum-hot-pressing. Translucent-transparent specimens could also be obtained by direct hot-pressing of hydroxides. Less success was found in such pressing of a basic carbonate powder. The lack of explosions in these pressings is attributed to thinner pressings and most of the outgassing occurring below 1000°C with limited pressure.

Final densification of MgO without additives generally starts from the center of the body. Limited quantities of carbonate and hydroxide impurities probably as liquid phases may play a role in this final densification. In fabrication with NaF and LiF, the main effect of hot-pressing may be primarily to bring about more intimate contact of particles

by enhanced interparticle sliding, supplemented by individual particle deformation made feasible by such sliding. The actual sintering mechanism occurring, whether or not pressure is applied, is probably enhanced diffusion along and across a grain boundary layer of fluoride-rich material. This is most likely due to liquid-phase sintering or defects due to solution of fluorine and not Li or Na when fluoride additives are used.

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